Anisotropic spin freezing in the S=1/2 zigzag ladder compound $SrCuO_2$

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(February 1, 2008)

Using magnetic neutron scattering we characterize an unusual low temperature phase in orthorhombic $SrCuO_2$. The material contains zigzag spin ladders formed by pairs of S=1/2 chains ($J = 180$ meV) coupled through a weak frustrated interaction ($|J'| \lesssim 0.1J$). For $T < T_{c1} = 5.0(4)$ K an elastic peak develops in a gapless magnetic excitation spectrum indicating spin freezing on a time scale $\delta t > \hbar/\delta E = 2 \cdot 10^{-10}$ s. While the frozen state has long range commensurate antiferromagnetic order along the chains ($\xi_c > 200c$) and a substantial correlation length ($\xi_a = 60(25)a$) perpendicular to the zigzag plane, the correlation length is only $\xi_b = 2.2(3)b$ in the direction of the frustrated interaction. We argue that slow dynamics of stripe-like cooperative magnetic defects in tetragonal $\mathbf{a}-\mathbf{c}$ planes yield this anisotropic frozen state.

PACS numbers: 75.10.Jm, 75.40.Gb, 75.50.Ee

Reduced dimensionality [1,2], geometrical frustration [3], and band formation [4] can suppress the critical temperature of magnets far below a cooperative energy scale such as the Curie-Weiss temperature. The resulting low temperature ordered phases have unconventional features that challenge conventional theories of magnetism. They include strongly reduced sublattice magnetization, abnormal sensitivity to low levels of disorder, and mean-field like critical behavior.

Quasi-one-dimensional magnetic dielectrics are excellent model systems in which to explore weakly ordered phases because a quantitative connection between the dynamic properties of the one-dimensional units and critical phenomena in the coupled system can be established [5–7]. Haldane spin-1 chains and other spin systems with a gap have a critical value for the inter-chain coupling $zJ_\perp \approx \Delta$ below which they remain disordered down to $T = 0$. Spin-1/2 chains on the other hand, are predicted to order even for vanishingly small non-frustrated inter-chain interactions. This is consistent with the low temperature long range order among weakly coupled spin-1/2 chains found in Sr_2CuO_3 and Ca_2CuO_3 [8].

In this letter we describe a different low temperature phase in closely related $SrCuO_2$, which contains linear spin-1/2 chains assembled pairwise in an array of weakly interacting zigzag ladders [9–15]. Though weak static sublattice magnetization does develop for $T < 5.0(4)$K $\approx 2.8 \cdot 10^{-3} J/k_B$, three dimensional long range order is absent for $T \gtrsim 10^{-4} J/k_B$. Specifically, we find a low temperature correlation length of only two lattice spacings along the direction of frustrated intra zigzag ladder interactions. We argue that slow dynamics of stripe-like defects in quasi-two-dimensional antiferromagnetic layers prevent the system from developing long range order.

Zig-zag ladders in $SrCuO_2$ are built from corner-sharing Cu-O chains with an exchange constant $J \approx 181(17)$ meV [13] stacked pairwise in edge-sharing geometry. The frustrating interaction between chains proceeds through $\approx 87.7°$ Cu-O-Cu bonds [10,16] and is expected to be weak and ferromagnetic $|J'| \lesssim 0.1J$. Field theory [17–19] and numeric simulations [19–21] for a pair of chains coupled like this predict that weak antiferromagnetic inter-chain coupling induces incommensurate correlations and a gap $\Delta \sim J\exp(-\alpha J/J')$ while the zigzag chain should remain gapless for ferromagnetic J' [18,19].

$SrCuO_2$ is centered orthorhombic (space group $Cmcm \equiv D^{17}_{2h}$) with lattice parameters $a = 3.556(2)$Å, $b = 16.27(4)$Å, $c = 3.904(2)$Å [11]. We index wave vector transfer in the corresponding simple orthorhombic reciprocal lattice. Nuclear Bragg reflections (h, k, l) are allowed for even $h + k$ and even l when $k = 0$. While there is no direct information about the magnitude of interactions between zigzag ladders, the structural features that determine them are similar to those in Sr_2CuO_3. Application of quantum Chain Mean Field (CMF) theory [7] to Sr_2CuO_3 yields an estimate for inter-chain interactions of $\overline{J_\perp} \approx k_BT_N/(1.28\sqrt{\ln(5.8J/k_BT_N)}) \approx 0.13$ meV, while according to classical [5] CMF $\overline{J_\perp} = 3(k_BT_N)^2/(8JS^2(S+1)^2) \approx 8 \cdot 10^{-4}$ meV.

The neutron scattering experiments were performed at the NIST Center for Neutron Research using cold and thermal neutron triple axis spectrometers. PG(002) reflections were used for monochromator and analyzer, supplemented by Be and PG filters. Our sample is a cylindrical rod ($\ell \approx 46$ mm, $D \approx 5$ mm, and $m = 3.875(5)$ g) grown by the Traveling Solvent Floating Zone (TSFZ) technique. Rocking curves about the $\mathbf{b}$ axis showed two roughly equal intensity peaks separated by $\approx 0.5°$ and each with a Full Width at Half Maximum (FWHM) $\approx 0.25°$. Experiments were performed with wave-vector transfer in the $(h, 0, l)$ and (h, k, h) reciprocal lattice planes. We used incoherent scattering from a vanadium

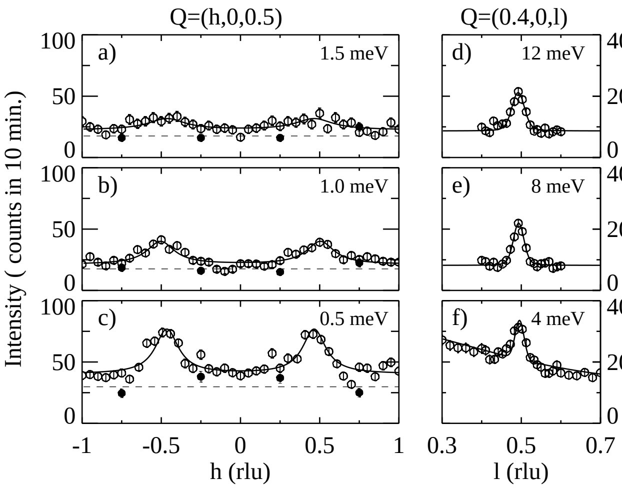

FIG. 1. Wave-vector dependence of inelastic magnetic scattering from $SrCuO_2$. (a)-(c) show data along $\mathbf{a}^*$ which is perpendicular to the zigzag ladders while (d)-(f) show data along the chains. (a)-(c) were collected on SPINS at $T = 0.35$K with $E_f = 5.1$ meV and collimations $80' - 80' - 240'$. (d)-(f) come from BT2 at $T = 12.5(5)$K with $E_f = 14.7$ meV and collimations $60' - 60' - 80' - 120'$. Increasing background in (f) comes from the direct beam.

rod in the same geometry as our $SrCuO_2$ sample to normalize the magnetic scattering cross section.

The defining characteristic of a quasi-one-dimensional spin system is an anisotropic dynamic correlation volume, which can be probed by inelastic magnetic neutron scattering. Fig. 1 shows constant energy scans along two perpendicular directions in the $(h, 0, l)$ plane for energy transfer 0.5 meV$< \hbar\omega <$ 14 meV. Scans along the chain direction (Fig. 1 (d)-(f)) reveal a resolution limited peak centered at $l = \frac{1}{2}$. The data yield an upper limit $\delta q \lesssim 0.01\mathbf{c}^*$ on any intrinsic FWHM of the peak. For comparison, the FWHM of the des Cloizeaux-Pearson continuum for each antiferromagnetic spin-1/2 chain at $\hbar\omega = 4$ meV is predicted to be $\delta q = (2\hbar\omega/\pi^2 J)c^* = 4.5 \cdot 10^{-3}$ and hence it is unresolved in our measurement. Fig. 1 (a)-(c) show scans along the $\mathbf{a}$ direction which is normal to the plane of the zigzag ladders. There we find peaks for $|h| \approx \frac{1}{2}$ which span the better part of the Brillouin zone and this provides evidence for short range dynamic antiferromagnetic correlations perpendicular to zigzag ladders. The correlation anisotropy between the two directions probed is $\delta q_a/\delta q_c > 10a^*/c^*$. While our measurements do not yield an energy scale associated with dispersion along $\mathbf{c}^*$ we found that modulation along $\mathbf{a}^*$ exists only for $\hbar\omega \lesssim 2$ meV.

Susceptibility, heat capacity, and μSR measurements indicate that static magnetic order develops below $T \sim$ 2K in $SrCuO_2$ [12]. Figure 2 shows the corresponding elastic magnetic neutron scattering, which we found at $\mathbf{Q} = \tau \pm \mathbf{Q}_m$ where τ is a reciprocal lattice vector, $\mathbf{Q}_m = (\frac{1}{2} + \epsilon, k, \frac{1}{2})$, $\epsilon = 0.006(1)$, and k is an integer. However, rather than being concentrated in a resolution limited

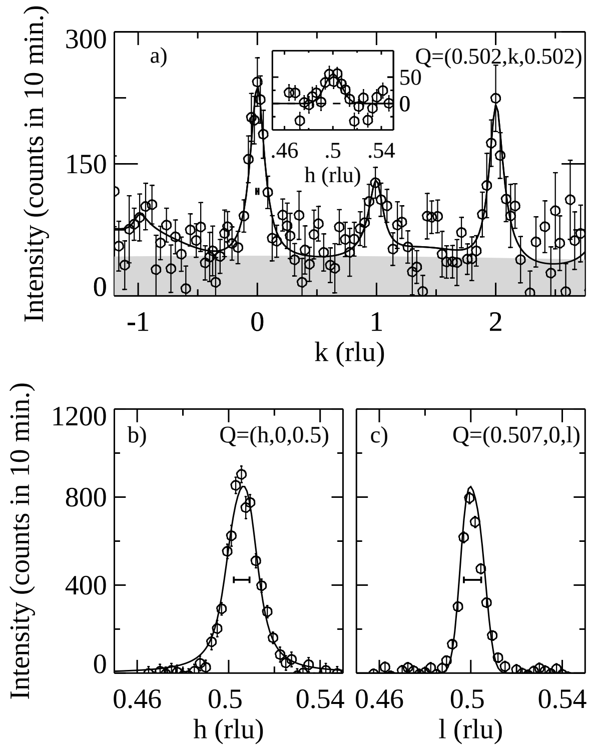

FIG. 2. (a)-(c) wave-vector dependence of the net elastic magnetic intensity around $\mathbf{Q} \approx (0.5, 0, 0.5)$ at T=0.35K along $\mathbf{b}^*$, $\mathbf{a}^*$ and $\mathbf{c}^*$ directions respectively. The background was measured at T=8K. Horizontal bars show calculated FWHM of the instrument resolution function. (a) BT2 and BT9 measurements with $E_f = 14.7$ meV and collimations $60' - 40' - 40' - 120'$. The shaded area shows k-independent "magnetic rod" intensity. The solid line shows Eq. (1) with optimized Fourier coefficients and multiplied by the squared magnetic form factor for Cu^{2+}. Insert shows scan across the rod at $k = 0.35$. (b), (c) SPINS data with $E_f = 3.7$ meV and collimations $80' - 40' - 240'$. Solid lines are fits to resolution convoluted Lorentzians.

Bragg peak, the signal has a characteristic distribution in reciprocal space, which shows that our sample does not have conventional three dimensional long-range magnetic order. The peak is sharpest in the $\mathbf{c}^*$ direction, wider and incommensurate in the $\mathbf{a}^*$ direction, and very broad along $\mathbf{b}^*$. Fig. 2 (a) and its inset also reveal a rod of elastic magnetic scattering extending along $\mathbf{b}^*$. Based on this information the frozen magnetic structure can be described as follows. Spins in each tetragonal $\mathbf{a} - \mathbf{c}$ plane are aligned antiferromagnetically with a superposed long wavelength modulation or defect structure in the $\mathbf{a}$ direction. Such planes are stacked with a correlation length of only a few times the lattice spacing along $\mathbf{b}$.

By fitting data in Fig. 2 to Lorentzians duly convoluted with the instrumental resolution function, the magnetic correlation lengths in the $\mathbf{a} - \mathbf{c}$ plane were determined to be $\xi_a = 60(25)a$ and $\xi_c \gtrsim 200c$. The peak position refined to $\mathbf{Q}_m = (0.506(1), 0.00(1), 0.500(1))$.

Note that the incommensurability along $\mathbf{a}^*$ was reproduced in several independent experiments. Moreover, we found an equivalent magnetic satellite from $\tau = (202)$ at $\mathbf{Q} = (1.494(3), 0.00(1), 1.500(1)) \approx \tau - \mathbf{Q}_m$.

The extremely short correlation length along $\mathbf{b}$ suggests analysis of scans along this direction in terms of a Fourier series:

$$\bar{S}^{\alpha\alpha}(\mathbf{Q}) = \frac{\langle S \rangle^2}{3}(1 + \frac{1}{N_\parallel}\sum_{j \neq j'} \mathcal{C}_{j,j'} \cos \mathbf{Q} \cdot (\mathbf{d}_j - \mathbf{d}_{j'})), \quad (1)$$

where j, j' index consecutive $\mathbf{a} - \mathbf{c}$ spin planes and $\mathcal{C}_{j,j'} = (1/N_\parallel) \sum_m \langle S_{\mathbf{d}_{j+2m}} \rangle \langle S_{\mathbf{d}_{j'+2m}} \rangle / \langle S \rangle^2$. For simplicity we have assumed that the frozen spin configuration is isotropic in spin space and an exponential decay of correlations between planes separated by distances of $2b$ and beyond. The line through the data in Fig. 2 shows the result of this fit. The correlation length extracted is $\xi_b = 2.2(3)b$. The correlation parameters $\mathcal{C}_{jj'}$ are listed in table 1.

$SrCuO_2$ is built from copper bilayers. Equivalent spins within a bilayer are displaced by $\mathbf{d}_1 - \mathbf{d}_0 = (0\delta\frac{1}{2})$ to form zigzag ladders. Bilayers are stacked in registry -ABABAB- where neighboring A and B type bilayers are separated by $\mathbf{d}_2 - \mathbf{d}_0 = (\frac{1}{2}\frac{1}{2}0)$. Table 1 shows that despite the proximity of planes that make up a bilayer, correlations between them are weak. This is experimental evidence for an effective decoupling between zigzag ladder rungs. Looking beyond a bilayer we see antiferromagnetic correlations between spins in shifted bilayers A and B ($\mathcal{C}_{0\bar{1}}, \mathcal{C}_{03}, \mathcal{C}_{0\bar{5}}, \mathcal{C}_{07} < 0$) and ferromagnetic correlations between spins in bilayers separated by multiples of $\mathbf{b}$ ($\mathcal{C}_{0\bar{3}}, \mathcal{C}_{0\pm 4}, \mathcal{C}_{05}, \mathcal{C}_{0\bar{7}} > 0$). Though they are separated by half the distance, nearest neighbor A-B correlations are significantly weaker than A-A correlations and this is evidence for frustrated inter-bilayer interactions. From the fit we also obtain a reliable value for the frozen moment at $T = 0.3$ K which turns out to be only a minute fraction of the full moment: $g < S >= 0.033(7)$ per Cu.

The temperature dependence of the squared frozen moment and the in-plane correlation parameters are shown in Fig. 3. The frozen staggered magnetization appears below $T_{c1} = 5.0(4)$K and initially increases in proportion to $(T_{c1} - T)^{2\beta}$ where $\beta = 0.46(12)$. Below an inflection point at $T_{c2} = 1.5(3)$K, $\langle S \rangle^2$ increases faster until saturating below $T \sim 0.5$K. Careful inspection of specific heat data [12] for $SrCuO_2$ reveal anomalies close to both T_{c1} and T_{c2}. While the peak position along the chain, l_0, is temperature independent, both the incommensurability and the Half Width at Half Maximum (HWHM), $\kappa_h = a/(\pi\xi_a)$ along $\mathbf{a}^*$, decrease by approximately a factor 2 below T_{c2}. It is useful to compare our results to those for Sr_2CuO_3 [8]. The critical temperature ($T_N = 5$ K) and intra-chain exchange constant ($J = 220$ meV) are similar for the two materials. Nonetheless, the moment in $SrCuO_2$ is almost twice smaller than in Sr_2CuO_3.

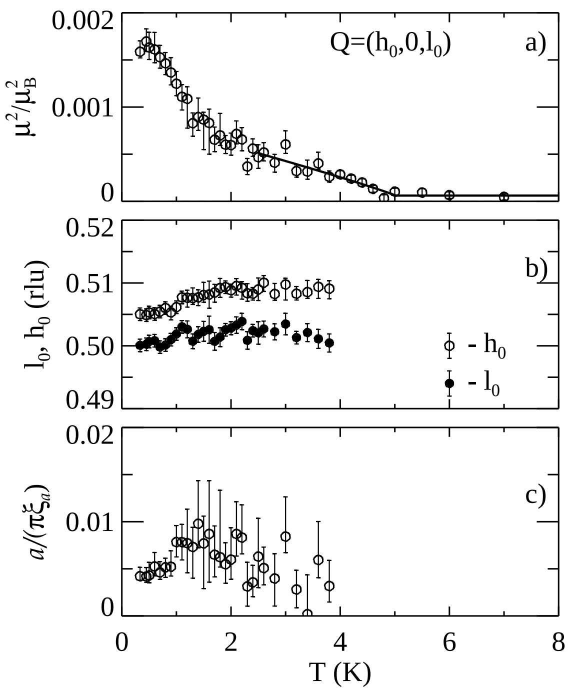

FIG. 3. Temperature dependencies of (a) the frozen sublattice magnetization squared, (b) the in plane wave vector ($\mathbf{Q} = (h_0.0.l_0)$), and (c) the inverse correlation length along $\mathbf{a}$. Data derived from h and l scans through the $(\frac{1}{2} + \epsilon 0 \frac{1}{2})$ elastic magnetic peak on SPINS using $E_f = 4.47$meV and collimations $80' - 80' - 240'$. The frozen moment in (a) is within error bars of our global average.

There is also a qualitative distinction between ordering in these materials; the frozen phase in $SrCuO_2$ is incommensurate along $\mathbf{a}$, while Sr_2CuO_3 has commensurate order [8]. Magnetic disorder along $\mathbf{b}$ is also unique to $SrCuO_2$. While this feature may be connected to quenched disorder, possibly from oxygen non-stoichiometry in our sample, the magnetic correlation length along $\mathbf{b}$ is easily an order of magnitude less than the defect spacing. $SrCuO_2$ therefore falls in the category of magnets which are either intrinsically disordered or display an extreme sensitivity to disorder. We shall argue that highly frustrated intra- and inter-zigzag ladder interactions are central to understanding these differences, and the anisotropic frozen state in general.

The main contribution to inter-zigzag ladder interactions along $\mathbf{a}$ comes from weak superexchange along Cu-O-O-Cu paths with two $\approx 90^\circ$ bonds. For each spin there are 12 such equivalent Cu-O-O-Cu paths to neighbors in the same $\mathbf{a}$–$\mathbf{c}$ plane; four to each nearest neighbor along $\mathbf{a}$, denote the corresponding exchange constant $J'_a > 0$, and one to each next nearest neighbor in diagonal $(1, 0, \pm 1)$ directions, $J''_a > 0$. As a consequence we expect that $J''_a \sim J'_a/4$ corresponding to a highly frustrated point for this lattice. Similar interactions exist in the $(1, \delta, \pm\frac{1}{2})$ directions between nearest neighbors in adjacent $\mathbf{a} - \mathbf{c}$ planes. In fact, it is evident that these

interactions as well as the inter-bilayer interactions all share the same frustrating zigzag geometry and all cancel at the mean-field level. In addition there may be other weak non-frustrated interaction favoring long range order. Experimental evidence for competing interactions in $SrCuO_2$ lies in the incommensurability of the magnetic peaks along the $\mathbf{a}^*$ direction. We note that the shift of the magnetic peak along $\mathbf{a}^*$ equals its HWHM not only at the lowest T but also as a function of $T \lesssim T_{c2}$. This indicates that we are dealing not with a periodic modulation superimposed on otherwise antiferromagnetic $\mathbf{a}-\mathbf{c}$ planes but a highly disordered or even random sequence of *frozen* stripe defects induced by these competing interactions.

Recent theoretical studies [6,22] have established that coupled S=1/2 chain systems can remain disordered at T=0 if interchain interactions are sufficiently frustrated. In the quasi-two-dimensional case which may be a good first approximation for $SrCuO_2$, disorder at T=0 could result from *instanton* topological defects created through quantum tunneling [22]. For *half-integer* or *odd* integer spin systems the disordered ground state is predicted to be degenerate and gapless while *even* integer spin systems should be gapfull. Our experimental results support a gapless phase for S=1/2.

At $T > 0$ topological disorder is enhanced through thermal creation of defects, leading to a reduced correlation length. In the coupled S=1/2 chain system we expect defects to be strongly anisotropic, taking the form of stripes extending along $\mathbf{c}$ between bands of phase shifted antiferromagnetic domains. For order to develop in a stack of $\mathbf{a}-\mathbf{c}$ planes, stripe defects in neighboring planes must move into registry. However, as mentioned above, the residual interactions which favor such ordering are either exceedingly weak or cancel at the mean field level. Thus it seems plausible that pinning and/or intrinsically slow dynamics of such stripe defects might lead to *spin freezing* instead of long range order.

In summary we have found an anisotropic spatially disordered frozen spin configuration among interacting zigzag spin-1/2 ladders in $SrCuO_2$. The magnetic correlation length along the short direction of the zigzag ladder is far less than the impurity spacing. Highly frustrated interactions both within the zigzag spin-1/2 ladders and between ladders, as well as slow dynamics and pinning of order-destroying stripe defects are likely reasons that $SrCuO_2$ behaves differently from the closely related linear chain system Sr_2CuO_3. Previous theoretical work on coupled S=1/2 chains has indicated the possibility of an intrinsic disordered phase [6,21,22]. Given our data it would be interesting to further explore this possibility with competing interactions of the specific type found in $SrCuO_2$.

We thank I. Affleck, G. Shirane, and A. J. Millis for useful discussions and R. Erwin for assistance during the experiments. Work at JHU was supported by the NSF through DMR-9453362. This work used instrumentation supported by NIST and the NSF through DMR-9423101.

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TABLE I. Correlations between spins in $\mathbf{a}-\mathbf{c}$ planes displaced by $\mathbf{d}_{j'}-\mathbf{d}_0$ with respect to each other. Coordinates are given in units of orthorhombic cell parameters. $\delta = 0.122$ [11] is the spacing in units of b between linear spin chains that form a zigzag chain. Error bars define intervals wherein χ^2 is statistically indistinguishable from its minimum value. "?" indicates correlations whose contributions to Eq. (1) cancel in a $(\frac{1}{2}k\frac{1}{2})$ scan.

j'	$\mathbf{d}_{j'}-\mathbf{d}_0$	$\mathcal{C}_{0,j'}$	j'	$\mathbf{d}_{j'}-\mathbf{d}_0$	$\mathcal{C}_{0,j'}$
1	$(0\delta\frac{1}{2})$	-0.09(6)	5	$(01+\delta\frac{1}{2})$	0.09(4)
-1	$(\frac{1}{2}\delta-\frac{1}{2}\frac{1}{2})$	-0.09(5)	-5	$(\frac{1}{2}\delta-\frac{3}{2}\frac{1}{2})$	-0.18(4)
±2	$(\frac{1}{2}\pm\frac{1}{2}0)$	?	±6	$(\frac{1}{2}\pm\frac{3}{2}0)$	?
3	$(\frac{1}{2}\frac{1}{2}+\delta\frac{1}{2})$	-0.19(5)	7	$(\frac{1}{2}\frac{3}{2}+\delta\frac{1}{2})$	-0.11(4)
-3	$(0\delta-1\frac{1}{2})$	0.06(5)	-7	$(0\delta-2\frac{1}{2})$	0.06(4)
±4	(0 ± 10)	0.23(3)			